

# PATENT SPECIFICATION

NO DRAWINGS

Inventors: HERMANN RATH, KARL BREDERECK, HORST RIECKERT, HANS TOEPFFER, OTTO TROSKEN, HANSWILLI VON BRACHEL and CHRISTIAN HEID

1,114,036



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Date of Application and filing Complete Specification 8 Nov. 1966.

No. 50020/66.

Application made in Switzerland (No. 15411) on 9 Nov., 1965.

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Int. Cl.: —D 06 p 1/30

## COMPLETE SPECIFICATION

Improving the Wet Fastness Properties of

### ERRATA

SPECIFICATION No. 1,114,036

Page 1, line 36, *delete* whole line

Page 5, line 30, the word following "the"  
*should read* "textile"

THE PATENT OFFICE  
5th July 1968

15 fabrics, fibres, and yarn, and more particularly, to a process and composition for treating sulphur-dyed cellulosic textiles to improve their wet fastness and their tensile strength. This invention also relates to novel textile products produced by the above process.

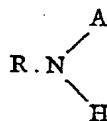
20 Canadian Patent No. 734,324 discloses a process for improving the wet fastness properties of cellulosic textile fibres and fabrics dyed or printed with sulphur dyes by after-treatment of the freshly prepared dyeings or prints, subsequent to short rinsing and prior to their oxidation, with polyfunctional substances that yield stable reaction products together with the dyestuffs.

30 In accordance with the present invention, we have found that it is possible to achieve greater improvements in the wet fastness properties of textile cellulosic materials which have been printed or dyed with sulphur dyes than heretofore known in the prior art. More specifically we have found that such improved wet fastness may be obtained by im-  
35 textile materials dyed with sulphur dyestuffs

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with a basic nitrogen compound, for example, in a suitable solvent, and then heating the mixture for a sufficient period of time to form a reaction product, after which the solvent may be removed from the product by distillation. The resultant reaction product is then applied to the dyed textile materials in a suitable manner, such as from an aqueous treating bath. The aqueous bath preferably may contain a basic compound, so that the textile materials are impregnated under alkaline conditions. After impregnation of the fabrics, they may be subjected to conventional finishing treatments.

Water-soluble, nitrogeneous bis- or poly- $\alpha,\beta$  - halohydrins suitable for use in the present invention are, for example, those obtained by reacting an epihalohydrin with ammonia or an amine of the general formula



SEE ERRATA SHEET ATTACHED

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## COMPLETE SPECIFICATION

### Process for Improving the Wet Fastness Properties of Textile Materials Dyed with Sulphur Dyestuffs

We, CASSELLA FARBWERKE MAINKUR AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of 6 Frankfurt/Main-Fechenheim, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the dyeing of fibrous cellulosic textile materials such as fabrics, fibres, and yarn, and more particularly, to a process and composition for treating sulphur-dyed cellulosic textiles to improve their wet fastness and their tensile strength. This invention also relates to novel textile products produced by the above process.

Canadian Patent No. 734,324 discloses a process for improving the wet fastness properties of cellulosic textile fibres and fabrics dyed or printed with sulphur dyes by after-treatment of the freshly prepared dyeings or prints, subsequent to short rinsing and prior to their oxidation, with polyfunctional substances that yield stable reaction products together with the dyestuffs.

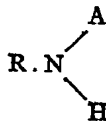
In accordance with the present invention, we have found that it is possible to achieve greater improvements in the wet fastness properties of textile cellulosic materials which have been printed or dyed with sulphur dyes than heretofore known in the prior art. More specifically we have found that such improved wet fastness may be obtained by im-

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pregnating the dyed or printed textile materials, after rinsing, and either prior to or subsequent to oxidation, with 0.1 to 5.0% by weight, based on the weight of the dry textile materials, of a water-soluble bis- or poly- $\alpha,\beta$ -halohydrin compound of those aliphatic or heterocyclic series containing at least one basic nitrogen atom.

The nitrogen-containing halohydrins of the present invention are prepared by combining a halohydrin, such as epichlorohydrin, with a basic nitrogen compound, for example, in a suitable solvent, and then heating the mixture for a sufficient period of time to form a reaction product, after which the solvent may be removed from the product by distillation. The resultant reaction product is then applied to the dyed textile materials in a suitable manner, such as from an aqueous treating bath. The aqueous bath preferably may contain a basic compound, so that the textile materials are impregnated under alkaline conditions. After impregnation of the fabrics, they may be subjected to conventional finishing treatments.

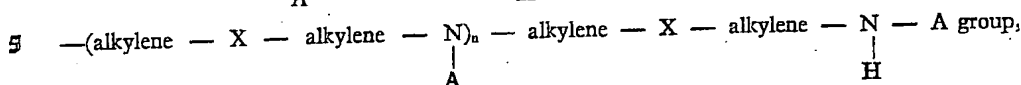
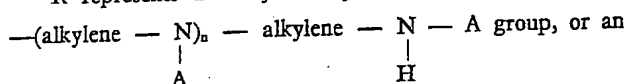
Water-soluble, nitrogeneous bis- or poly- $\alpha,\beta$ -halohydrins suitable for use in the present invention are, for example, those obtained by reacting an epihalohydrin with ammonia or an amine of the general formula



SEE ERRATA SLIP ATTACHED

wherein A represents hydrogen or an alkyl or hydroxyalkyl group of from 1 to 5 carbon atoms; and

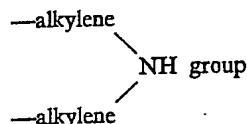
R represents an alkyl or hydroxyalkyl group of from 1 to 5 carbon atoms, an



wherein

x may be oxygen or sulphur and  
n is an integer from 0 to 5;

or wherein R and A may together represent an



10 Examples of amines corresponding to the above formula which may be used in the present invention are: methylamine, ethylamine, propylamine, isopropylamine, butylamine, isobutylamine, monohydroxyethylamine, monohydroxypropylamine, ethylenediamine, diaminopropanes, diaminobutanes, diaminohexanes, 3,3' - diaminodipropyl ether, piperazine, monohydroxyethyl - ethylene diamine, dihydroxyethyl - ethylene diamine, diethylene triamine, dipropylene triamine, triethylene tetramine.

In addition to improved wet fastness properties, the water-soluble, nitrogenous bis- or poly -  $\alpha, \beta$  - halohydrins of the present invention also achieve a substantial reduction in loss of tensile strength which may occur during the storage of textile materials dyed or printed with sulphur dyes, and in particular, with Sulphur Black.

30 Unlike the above-mentioned Canadian Patent No. 734,324, the improvement of the wet fastness properties according to the present invention is achieved even when the aftertreatment with the water-soluble, nitrogenous bis- or poly -  $\alpha, \beta$  - halohydrins is carried out subsequent to oxidation of the dyed or printed material with, for example, a solution of dichromate in acetic acid.

The following examples are given for the purpose of illustrating the present invention. Unless otherwise stated, temperatures are given in degrees Centigrade and percentages are percentages by weight based on the dry weight of the textile material to be dyed.

#### EXAMPLE 1:

45 Cotton fabric is dyed in a conventional dye bath containing 5% Immedial Supra Yellow GWL (Colour Index: Sulphur Yellow 5, constitution described in Collection Czechoslov. Chem. Commun. Vol. 27 (1962), page 1533/48), 3.75 g./l. crystallised sodium sulfide, 4 g./l. calcined sodium carbonate and

10 g./l. calcined Glauber's salt (liquor ratio 1:20). After rinsing, the fabric is introduced into a liquor containing 3% of a reaction product of ammonia and epichlorohydrin, the preparation of which is described below. By the addition of a sodium carbonate solution the liquor is adjusted to a pH of 10, then heated to 90—95° in the course of 20 minutes and kept at this temperature for 10 minutes. Subsequently, the fabric is thoroughly rinsed.

The examination of the fastness to washing with perborate, made in accordance with DIN 54015 (German Industrial Standards Method 54015), and the fastness to boiling with sodium carbonate, made in accordance with DIN 54031, indicates a substantially better result than that of a similarly dyed fabric without aftertreatment or one which is aftertreated in accordance with the above-mentioned Canadian Patent No. 734,324. The fastness to washing in the presence of reducing substance, for example, dextrin, is also considerably improved in the case of the cotton fabric aftertreated as disclosed in Example 1.

The reaction product used as the aftertreating agent is prepared in the following manner:

To a solution of 185 g. epichlorohydrin in 200 c.c. methanol at 25—30° is added, dropwise, over a period of 3 hours, a solution of 17 g. of ammonia in 200 c.c. of methanol. The mixture is stirred for 2 hours at 25—30°, heated to 70° over a 3 hour period, and kept at this temperature for 2 additional hours. The methanol is removed by vacuum distillation at 50—60° to produce 202 grams of a highly viscous oil reaction product that is easily soluble in water. For further purification, the product may be repeatedly dissolved in methanol and precipitated with ether.

A similarly effective aftertreatment product is obtained by an analogous reaction of

277 g. epichlorohydrin, dissolved in 300 c.c. methanol, with a solution of 17 g. ammonia in 200 c.c. methanol.

#### EXAMPLE 2:

5 Cotton fabric is dyed in the usual manner in a dyebath containing 4% Hydrogen Blue R for Sol (Colour Index: Vat Blue 43, CI No. 53630), 9 c.c./l. sodium hydroxide solution of 33° Bé, and 4 g./l. hydrosulfite (liquor ratio 1:20). After rinsing the fabric, an aqueous solution having a pH of 10 and containing 30 g./l. of a reaction product of n-butylamine and epichlorohydrin, prepared as indicated below, is padded onto the fabric in such a manner that 2% of the product goes onto the fabric. Thereupon, the material is steamed for 2 minutes, thoroughly rinsed, and finished. The treated fabric, when compared with similarly dyed fabrics not after-treated or those treated in accordance with the Canadian Patent, exhibits substantially improved wet fastness properties and, in particular, a good fastness to boiling with sodium carbonate and to washing with peroxide.

25 The aftertreatment reaction product may be prepared as follows: A solution of 73 g. butylamine in 100 c.c. ethanol, at 25°, is slowly added, dropwise, to 185 g. epichlorohydrin. Thereafter, the solution is heated to 60—65° over a 2 hour period and kept at this temperature for a further 2 hours. Subsequently, the ethanol is distilled off from the solution and the limpid yellowish oil reaction product obtained is easily soluble in water.

A product having a similar effect may be obtained by reacting in an analogous manner 61 g. monoethanol-amine with 185 g. epichlorohydrin.

#### EXAMPLE 3:

40 A cellulosic fabric is dyed in usual manner in a dyebath containing 8% Indocarbon CL for Sol (Colour Index: Sulphur Black 11, CI No. 53290), 8 g./l. crystallised sodium sulfide, 8 g./l. calcined sodium carbonate, and 20 g./l. calcined Glauber's salt (liquor ratio 1:10). After rinsing, the fabric is treated in a liquor containing a 2% reaction product of a diamine and epichlorohydrin, prepared as described below. The liquor, which was adjusted to a pH of 10 by addition of sodium carbonate solution, is then heated to 90—95° over a period of 30 minutes and kept at this temperature for 10 additional minutes. After thorough rinsing, the treated fabric is finished in the usual manner and possesses wet fastness properties, particularly those in respect to washing in the presence of dextrin, which are substantially

improved over those of a similarly dyed fabric which is not aftertreated or one which is aftertreated in accordance with the Canadian Patent.

For the aftertreatment of the above-dyed fabric, the following reaction products may be employed: epichlorohydrin and ethylene diamine in a molar ratio of 2:1, 3:1 and 4:1; also the corresponding products from the reaction of epichlorohydrin with 1,3 - diaminopropane, 1,4 - diaminobutane, 1,6 - diaminohexane, or 3,3'-diaminodipropyl ether; additionally, the reaction product of 3 mols epichlorohydrin with 1 mol monohydroxy-ethylethylene diamine or with N,N' - bis-(3 - chloro - 2 - hydroxypropyl) - piperazine can be used.

These reaction products may be prepared in the following manner:

A solution of 1 mol of the amine in 150 c.c. water is slowly added, dropwise, at room temperature, to the required amount of epichlorohydrin. The mixture is then heated to 60—70° in the course of 2 to 3 hours and the reaction is terminated by 2 hours' heating at this temperature. After elimination of the water by distillation under reduced pressure, the above reaction products are obtained in their pure form.

#### EXAMPLE 4:

A cotton fabric is dyed in a 90° dyebath containing 10% Hydrosol Black B (Colour Index: Solubilised Sulphur Black, CI No. 53186), 2.5 g./l. calcined sodium carbonate, 2.5 g./l. sodium sulphhydrate and 10 g./l. calcined Glauber's salt (liquor ratio 1:20). After rinsing, the fabric is treated for 10 minutes at 30° in a liquor containing 4% of a reaction product of 4 mols epichlorohydrin and 1 mol 3,3' - diamino - dipropyl ether, and 2% sodium carbonate. Subsequently, the liquor is heated to 90° in the course of 20 minutes and then kept at this temperature for a further 10 minutes. Thereafter, the fabric is rinsed, acidified with 2 c.c./l. acetic acid of a 60% concentration, and dried.

To test the storability, ropes of an untreated dyed material and of a dyed material aftertreated in the manner described above are treated for six hours, at 135°, in a damp atmosphere, according to the AATCC-method B/93 (AATCC Annual Register 1963) and the tensile strength is determined both prior and subsequent to this treatment. The results of the tests indicated below show that the rope aftertreated in accordance with the present invention possesses and retains a higher tensile strength than a similarly dyed untreated rope.

	Cotton Rope Dyed with 10% Hydrosol Black B	Tensile Strength in gms. Prior to Artificial Aging	Tensile Strength in gms. Subsequent to Artificial Aging	Residual Tensile Strength in % After Artificial Aging
5	a) untreated	594	122	21
10	b) aftertreatment according to Example 4	633	530	84

## EXAMPLE 5:

Cotton cheeses are dyed in a 90° dyebath containing 10% Indocarbon CL conc. (Colour Index: Sulphur Black II, CI No. 53290), 30 g./l. crystallised sodium sulfide, 4 g./l. calcined sodium carbonate and 20 g./l. calcined Glauber's salt (liquor ratio 1:10). The dyed material is rinsed with cold water, filtered off with suction, and treated in a liquor (ratio of 1:10) containing 3% (related to the dry weight of the fabric) of a reaction product of 5 mols epichlorohydrin and 1 mol diethylene triamine, and 1% calcined sodium carbonate, during which time the temperature is raised from 30° to 90° in the course of 20 minutes and then kept at 90° for 10 minutes; subsequently, the fabric is thoroughly rinsed. The cheeses thus obtained possess very good wet fastness properties, in particular a very good fastness to washing with peroxide and dextrin, as well as a good fastness to storing, which property is also retained when the dyeing is aftertreated in an acid liquor or brightened.

In place of the above-mentioned reaction product, the following products can likewise successfully be employed: reaction products of 5 mols epichlorohydrin and 1 mol dipropylene triamine, 6 mols epichlorohydrin with 1 mol triethylene tetramine, 7 mols epichlorohydrin with 1 mol tetraethylene pentamine, and 8 mols epichlorohydrin with 1 mol pentaethylene hexamine.

These products are prepared in accordance with the methods described in the above examples.

## EXAMPLE 6:

A cotton fabric is dyed in a dyebath containing 5% Hydrosol Yellow RR (Colour Index: Solubilised Sulphur Yellow 2, CI No. 53121), 3.75 g./l. crystallised sodium sulfide, 4 g./l. calcined sodium carbonate, and 10 g./l. Glauber's salt (liquor ratio 1:20). After rinsing, the fabric is introduced into an aqueous bath containing 3% of one of the reaction products mentioned in the second paragraph of Example 3, and 1.5% calcined sodium carbonate. The temperature of the bath is raised from 30° to 90° in the course of 10 minutes and then kept at 90° for 5 minutes. The fabric is then removed and

thoroughly rinsed. The thus dyed and after-treated fabric yields a satisfactory result in washing in accordance with AATCC Test Method No. 3, as well as a substantially improved fastness to washing in accordance with DIN 54011 and peroxide washing in accordance with DIN 54015 when compared with an untreated fabric or one treated in accordance with the Canadian Patent. The fabric which is not aftertreated, but is oxidised in the usual manner with a solution of dichromate in acetic acid, stains to a high extent an undyed fabric which is concurrently washed in accordance with AATCC Test Method No. 3. The result of the AATCC Test Method No. 3 washing of the after-treated fabric is also satisfactory when the reaction product is applied subsequently to oxidation of the fabric with a solution of dichromate in acetic acid.

## EXAMPLE 7:

A cotton fabric is dyed in a dyebath containing 4% Hydrosol Supra-Blue B (Colour Index: Solubilised Sulphur Blue 7, CI No. 53441), 3 g./l. crystallised sodium sulfide, 4 g./l. calcined sodium carbonate and 10 g./l. calcined Glauber's salt (liquor ratio 1:20). After rinsing and squeezing off, the fabric is treated in a liquor containing 3% of the reaction product mentioned in the first paragraph of Example 4 and 1.5% calcined sodium carbonate. The temperature of the liquor is raised from 30° to 60° in the course of 10 minutes and then kept at 60° for a further 10 minutes. Subsequently, the fabric is thoroughly rinsed. The dyed and after-treated fabric yields a satisfactory result in washing according to AATCC Test Method No. 3, as well as a substantially improved fastness to washing in accordance with DIN 54011 and peroxide washing in accordance to DIN 54015 when compared with fabrics which are not aftertreated or oxidised in the usual manner with a solution of dichromate in acetic acid.

## WHAT WE CLAIM IS:—

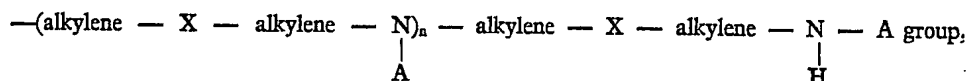
1. Process for improving the wet fastness properties of dyeings and prints obtained with sulphur dyestuffs characterised by impregnating the dyed or printed materials with 0.1 to

- 5% by weight, related to the dry weight of the materials, of a water-soluble bis- or poly- $\alpha,\beta$ -halohydrin compound of those aliphatic or heterocyclic series containing at least one basic nitrogen atom and thereafter subjecting the cellulosic material to conventional finishing treatments.

2. Process according to claim 1 charac-

wherein A represents hydrogen or an alkyl or hydroxyalkyl group of from 1 to 5 carbon atoms; and

- 15 R represents an alkyl or hydroxyalkyl group of from 1 to 5 carbon atoms, an  
 —(alkylene — N)<sub>n</sub> — alkylene — N — A group, or an

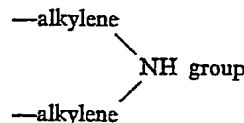


wherein

x may be oxygen or sulphur and  
 n is an integer from 0 to 5;

20

or wherein R and A may together represent an



3. Process according to claim 1 characterised by impregnating the textile cellulosic materials under alkaline conditions.
- 25 4. Process according to claim 1 characterised by impregnating the textile cellulosic materials prior to the oxidation of the dyeing or print.
- 30 5. Process according to claim 1 characterised by impregnating the textile cellulosic materials subsequent to the oxidation of the dyeing or print.
- 35 6. Process for improving dyeings and prints obtained with sulphur dyestuffs as claimed in any of claims 1 to 5 characterised by
- utilising the reaction product of epichlorohydrin and ethylene diamine.
7. Process for improving dyeings and prints obtained with sulphur dyestuffs substantially as described in any of the specific Examples.
- 40 8. Textile cellulosic materials dyed or printed with sulphur dyestuffs, said dyeings and prints being improved according to the process as claimed in any of the claims 1 to 7.
- 45

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